

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Patent Application of

Date: November 6, 2008

Applicants: Bednorz et al.

Docket: YO987-074BZ

Serial No.: 08/479,810

Group Art Unit: 1751

Filed: June 7, 1995

Examiner: M. Kopec

For: NEW SUPERCONDUCTIVE COMPOUNDS HAVING HIGH TRANSITION
TEMPERATURE, METHODS FOR THEIR USE AND PREPARATION

Mail Stop: Appeal Brief – Patents
Commissioner for Patents
United States Patent and Trademark Office
P.O. Box 1450
Alexandria, VA 22313-1450

REPLY TO EXAMINER'S ANSWER

Dated 08/20/2008

Supplement 3

ARGUMENT

As stated in Brief Volume 1, for example at pages 207 - 208, lines 3 -5, the Examiner cites the article of Schuller which refers to the discovery of superconductivity in MgB_2 .

Applicants bring to the Board's attention that MgB_2 was made at least as early as 1954, more than 30 years prior to Applicants' discovery of High T_c superconductivity, as reported in the following article:

The Preparation and Structure of Magnesium Boride, MgB_2

Morton E. Jones and Richard E. Marsh

J. Am. Chem. Soc.; **1954**; 76(5) pp 1434 - 1436; DOI: [10.1021/ja01634a089](https://doi.org/10.1021/ja01634a089)

A copy of this article is attached herewith designated as Brief Attachment BM.

Thus persons of ordinary skill in the art knew how to make MgB_2 long before Applicants' discovery and as noted in the Brief Volume 1 in the last sentence of page 126 it has been well known how to test a material for superconductivity since the discovery of superconductivity in 1911. Thus as note in Reply Supplement 2 in the paragraph bridging pages 5 and 6 it would have been obvious for a person of ordinary skill in the art after Applicants' discovery to try MgB_2 to determine if it had a T_c greater than or equal to 26 K.

Applicants submitted the attached Article (designated in Brief Attachment BM) with the Eighteenth Supplemental Response After Final Rejection concurrent with this Reply Supplement 3 and thus it has not been entered when this Reply Supplement 3 was filed. If the Examiner does not enter the Eighteenth Response After Final, Applicants respectfully request the Bard to take judicial notice of that persons of skill in the art knew how to make MgB_2 to long before Applicants' discovery, since this is information is known to persons of skill in the art and should be known to the Examiner who cited the Schuller article which refers to MgB_2 .

Thus following *In re Fisher* since applicants have enabled MgB_2 , whether or not it is unobvious in view of Applicants' teaching, Applicants should be allowed a claim that dominates it. As stated by Brief Volume 1 page 237, lines 3 -4, "It is thus clear following the Supreme Court decision in *Minerals Separation, Ltd. v. Hyde*, 242 U.S. 261 that all of Applicants' claims are enabled."

Applicants request the Board to reverse the rejection of all claims rejected under 35 USC 112, first paragraph, as not being enabled.

The Appendix to this Reply Supplement 3 lists an addition to the Brief to reflect the addition of Brief Attachment BM added by the Eighteenth Supplemental Response after Final Rejection submitted herewith.

Please charge any fee necessary to enter this paper and any previous paper to deposit account 09-0468.

Respectfully submitted,

/Daniel P Morris/
Dr. Daniel P. Morris, Esq.
Reg. No. 32,053
(914) 945-3217

IBM CORPORATION
Intellectual Property Law Dept.
P.O. Box 218
Yorktown Heights, New York 10598

APPENDIX TO REPLY SUPPLEMENT 3

Addition to the Brief

At the bottom of page 17 of Brief Volume 1 add the following paragraph:

18) The Response After Final Rejection submitted 11-042008 entitled "Eighteenth Supplemental Response" has not been responded to with an Advisory Action as of the submission of this Corrected Appeal Brief.

BRIEF ATTACHEMENT BM

[CONTRIBUTION NO. 1862 FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY]

The Preparation and Structure of Magnesium Boride, MgB_2

BY MORTON E. JONES AND RICHARD E. MARSH

RECEIVED NOVEMBER 19, 1953

A compound MgB_2 has been prepared by heating the elements in an atmosphere of hydrogen. An X-ray diffraction investigation of powder samples has shown the compound to be isomorphous with AlB_2 ; the lattice constants of the hexagonal unit cell are $a_0 = 3.0834$ and $c_0 = 3.5213$ Å. The interatomic distances in MgB_2 and in other borides with the AlB_2 structure are discussed in terms of metallic bonds and electron transfer, and a value of 0.77 Å. has been assigned as the normal single-bond radius for boron in these compounds.

Introduction

When metallic magnesium and boric oxide are heated in an atmosphere of hydrogen, products are formed which yield, on acid hydrolysis, small quantities of boron hydrides, principally B_4H_{10} . In 1914 Ray¹ reported the presence of a magnesium boride in the products and obtained an analysis conforming to the formula Mg_3B_2 . Stock² has postulated that this boride might be the component which undergoes acid hydrolysis to the boron hydrides. He also reported the presence of an intermediate $\text{Mg}(\text{B}_4\text{O}_6)$, which was isolated as the potassium salt; this indicated that the boron atoms might be arranged in B_4 groups, and hence that magnesium boride might conform to the formula Mg_6B_4 . Because of the interesting relationship between these possible B_4 groups and the B_4H_{10} molecule (the structure of B_4H_{10} is being investigated in these laboratories), the preparation and investigation of the crystal structure of magnesium boride were undertaken.

Experimental

Commercial powdered boron (99.05%) was heated with a piece of magnesium (99.7%) larger than required by the stoichiometry of Mg_3B_2 in a MgO -coated iron crucible to about 800° for one hour; a current of hydrogen was passed through the crucible throughout the heating to minimize the formation of oxides and nitrides. After the sample had cooled, the excess magnesium, which was in the form of a metallic button, was removed and samples of the remaining black powder were sealed into thin-wall soft glass capillaries about $1/4$ mm. in diameter. X-Ray powder photographs, using nickel-filtered $\text{CuK}\alpha$ radiation, were prepared in a Straumanis-type Norelco powder camera of nominal radius $180/\pi$ mm.; two double-film exposures were made. A second preparation of the compound was photographed in the same manner. The positions of the diffraction lines were carefully measured with a steel scale and the intensities were estimated visually by the multiple-film technique. A film factor of 3.7 was used to relate intensities of each pair of photographs.

Structure Determination

Values of $\sin^2 \theta$ were calculated for all of the observed lines, and 25 out of the 31 lines were indexed on the basis of a hexagonal lattice. Of the remaining six weak lines, one had a macro-crystalline appearance and corresponded in position to the strong 200 reflection of magnesium, while the other five lines showed changes of intensity relative to the main pattern between the two different preparations, and were therefore assigned to an impurity that has remained unidentified. Preliminary values of a_0 and c_0 , chosen on the basis of the observed values of $\sin^2 \theta$, were refined by a least square

treatment. The resultant cell parameters and probable errors are

$$a_0 = 3.0834 \pm 0.0003 \text{ Å.}$$

$$c_0 = 3.5213 \pm 0.0006 \text{ Å.}$$

using $\lambda = 1.5418$ Å. for $\text{CuK}\alpha$. Standard deviations were obtained from the residuals and coefficients of the normal equations in the least squares treatment.³

A cell of this size is certainly too small to contain the three magnesium and two boron atoms corresponding to the previously reported formula Mg_3B_2 . Two alternatives are possible: either the formula approximates Mg_3B_2 and the structure is of a random type, or the composition differs from Mg_3B_2 , with fewer atoms per unit cell. The similarity of the cell constants to those reported for AlB_2 ⁴ indicated that the two compounds might be isomorphous, and structure factors were calculated on this basis, using the atomic form factors of James and Brindley.⁵ The atomic positions are 1 Mg at (000) and 2 B at $(1/3, 2/3, 1/2)$, $(2/3, 1/3, 1/2)$.

A comparison of F_{obsd} and F_{calcd} for all reflections within the sphere of copper radiation is given in Table I, along with observed and calculated values of $\sin^2 \theta$. The F_{obsd} values were reduced to an absolute scale by application of an empirical factor, and the F_{calcd} values include the empirical temperature factor $e^{-1.04 \sin^2 \theta / \lambda^2}$. For the unresolved (004, 203) doublet, values are given for $G^2_{\text{obsd}} = I/kLp$ and for $G^2_{\text{calcd}} = (mF^2_{\text{calcd}})_{004} + (mF^2_{\text{calcd}})_{203}$, where I is the observed intensity, k is the scale factor, L and p are Lorentz and polarization factors and m is the multiplicity of the appropriate reflection. Excluding this doublet and the unobserved 003 reflection, the value for $R = \sum ||F_{\text{obsd}}| - |F_{\text{calcd}}|| / \sum |F_{\text{obsd}}|$ is 0.105.

The density calculated on the basis of two boron atoms and one magnesium atom in the unit cell is 2.633; the density observed by the flotation method is 2.62. The compound is thus established as being MgB_2 .

A search for MgB_2 was made in the products of the reaction between Mg and B_2O_3 . The preparation was carried out by the method described by Stock² and powder photographs of the products were made. The strong lines on the photograph

(3) E. T. Whittaker and G. Robinson, "The Calculus of Observations," Blackie and Son, Ltd., London, 1937, Chap. IX.

(4) W. Hofmann and W. Janicke, *Z. physik. Chem.*, **B31**, 214 (1936).

(5) R. W. James and G. W. Brindley, from "Internationale Tabellen zur Bestimmung von Kristallstrukturen," Vol. II, Gebrüder Borntraeger, Berlin, 1935, p. 571.

(1) R. C. Ray, *J. Chem. Soc.*, **105**, 2162 (1914).

(2) A. Stock, "Hydrides of Boron and Silicon," Cornell University Press, Ithaca, N. Y., 1933, Chapt. 3 and 28.

TABLE I
 DIFFRACTION DATA FOR MgB_2

<i>hkl</i>	$\text{Sin}^2\theta_{\text{obsd}}$	$\text{Sin}^2\theta_{\text{calcd}}$	F_{obsd}	F_{calcd}	
001	0.0478	0.0479	2.2	3.8	
100	.0834	.0833	5.9	6.2	
101	.1313	.1313	9.3	9.7	
002	.1918	.1917	10.7	10.4	
110	.2501	.2500	9.9	9.5	
102	.2753	.2751	4.1	4.3	
111	.2980	.2980	2.9	2.6	
200	.3334	.3334	4.5	3.9	
201	.3809	.3813	6.4	6.4	
0034314	<3.0	2.0	
112	.4416	.4418	6.8	7.2	
103	.5151	.5147	4.6	5.4	
202	.5260	.5251	2.0	2.8	
210	.5841	.5834	3.5	2.6	
211	.6310	.6313	5.3	4.7	
113	.6815	.6814	1.2	1.2	
300	.7499	.7501	5.0	5.0	
203	.7644	.7647	$G^2 = 184$	4.0	$G^2 = 239$
004		.7669		4.9	
212	.7749	.7751	1.6	1.9	
301	.7994	.7980	1.2	1.2	
104	.8495	.8502	1.2	1.6	
302	.9410	.9418	2.9	4.2	

agree in position and intensity with those of MgO , and two of the weak lines correspond to two of the three strongest lines of the MgB_2 pattern (002 and 110). The other strong line of MgB_2 , 101, is degenerate in position with the strong 200 line of MgO . There is thus some evidence that the boride formed in the reaction between Mg and B_2O_3 is MgB_2 rather than Mg_3B_2 ; furthermore, since in our other preparations MgB_2 was formed in an excess of magnesium, it seems doubtful that Mg_3B_2 is a stable compound.

containing metal atoms of differing properties affords an opportunity to attempt to correlate the observed internuclear separations on the basis of present-day theories of the bonding properties of metals. In this regard, we have chosen to apply Pauling's system of metallic radii, appropriately corrected for electron transfer, to the observed interatomic distances in these borides. The method of application is as follows.

On the basis of Pauling's equation relating bond number n with observed internuclear separation⁸

$$D_1 - D_n = 0.6 \log n$$

where D_1 is the sum of the single-bond radii assigned to the two atoms involved in the bond and D_n is the observed internuclear separation, there is, for any value assigned to the single-bond radius of the metal atom in a compound MB_2 , only one value for the single-bond radius of boron which will result in the total calculated valences of the atoms being equal to the number of valence electrons present in the compound. Furthermore, the single-bond radius assigned to the metal atom should be consistent with the valence calculated for that atom, and which may differ from the normal valence in view of electron transfer. This is essentially the method used by Hedberg⁹ in his discussion of boron hydrides and related boron compounds.

The single-bond radii for the metal atoms (other than magnesium and aluminum) were chosen according to Pauling¹⁰ with appropriate corrections for any assumed electron transfer and resultant change in d-character of the bonds. The single-bond radii for magnesium and aluminum were calculated from the empirical formula

$$R_1 = 1.759 - 0.055z - 0.488p$$

where z is the number of outer electrons in the

 TABLE II
 LATTICE PARAMETERS AND BOND NUMBERS FOR COMPOUNDS OF THE TYPE MB_2

M	Mg	Al	Ti	V	Cr	Zr	Nb	Mo	Ta
a_0 (Å.)	3.0834	3.00	3.030	2.998	2.969	3.170	3.088	3.05	3.078
c_0 (Å.)	3.5213	3.245	3.223	3.057	3.066	3.532	3.304	3.113	3.265
B-B (Å.)	1.780	1.73	1.749	1.731	1.714	1.830	1.783	1.76	1.777
B-M (Å.)	2.503	2.37	2.378	2.309	2.300	2.543	2.431	2.35	2.413
M-M (Å.)	3.083	3.00	3.030	2.998	2.969	3.170	3.088	3.05	3.078
v_M	3.22	3.60	4.38	4.68	4.80	4.46	4.98	5.34	5.00
v_B	2.39	2.70	2.81	3.16	3.60	2.77	3.01	3.33	3.00
$r_1(\text{M})$	1.298	1.236	1.292	1.254	1.233	1.393	1.349	1.326	1.339
$r_1(\text{B})$	0.774	0.756	0.750	0.753	0.777	0.797	0.771	0.760	0.767
n (B-B)	0.410	0.433	0.385	0.422	0.541	0.404	0.397	0.397	0.394
n (B-M)	0.191	0.234	0.275	0.314	0.329	0.258	0.303	0.356	0.308
n (M-M)	0.154	0.132	0.181	0.152	0.145	0.229	0.224	0.178	0.215

Discussion

MgB_2 is the ninth metallic boride now known to possess the AlB_2 structure. Besides AlB_2 , the compounds TiB_2 , VB_2 , CrB_2 , ZrB_2 , NbB_2 and TaB_2 have been reported by Kiessling,⁶ while Bertant and Blum⁷ have reported on MoB_2 . In Table II there are given the lattice parameters and the interatomic distances in these nine borides.

The existence of these nine isostructural borides

neutral atom ($= Z - 10$) and p is the p-character of the bonds.⁸ In this regard, the values chosen for d- or p-character were interpolations between values for neighboring atoms; thus, the bond orbitals of titanium, which has an assumed valence of 4.4 (the excess over 4.0 being attributed to electron transfer), were given a d-character interpolated between the values 0.27 and 0.35 assigned

(6) R. Kiessling, *J. Electrochem. Soc.*, **98**, 166 (1951).

(7) F. Bertant and P. Blum, *Acta Cryst.*, **4**, 72 (1951).

(8) L. Pauling, *This Journal*, **60**, 542 (1947).

(9) K. Hedberg, *ibid.*, **74**, 3486 (1952).

(10) L. Pauling, *Proc. Roy. Soc. (London)*, **196A**, 23 (1949).

to bond orbitals of neutral titanium and neutral vanadium, respectively.

In Table II there are given the final calculated values for the boron single-bond radius for each of the compounds, as well as the assumed valences of each atom and the calculated bond numbers. The average value for the single-bond radius of boron is 0.767 Å., with an average deviation of 0.011 Å.

ADDED IN PROOF.—Russell, *et al.*,¹¹ have just published a short report of their investigations on the magnesium-boron system. Their results are in essentially exact agreement with ours. The values which they report for lattice parameters of MgB_2 are $a_0 = 3.084 \pm 0.001$ Å., $c_0 = 3.522 \pm 0.002$ Å.; in addition, they find evidence for three other crystalline phases, one apparently being MgB_4 . These other phases doubtless correspond to the unidentified impurity in our preparations.

The single-bond radius of boron might be expected to vary inversely with the valence of boron, as is observed for other atoms. Indeed, if a least-squares line is passed through the nine points representing a plot of single-bond radius of boron against v_B , this line may be expressed in the form $R_1(B) = A + C(3 - v_B)$; best values of A and C are 0.767 and 0.004, with the coefficient C being positive as predicted. However, the calculated standard deviation in C , 0.016, is so large as to make even the sign of C unreliable.

It should be pointed out that the calculated single-bond radius for boron in each compound is dependent upon the single-bond radius chosen for the other atom, which in turn is very sensitive to the amount of p- or d-character assigned to the bond orbitals. Furthermore, there is little valid reason to suppose that the d-character of bond orbitals of charged atoms can be accurately determined by simple interpolation. Thus, the com-

pounds NbB_2 and TaB_2 , which give evidence of little electron transfer, yield single-bond radii for boron very close to the average value 0.77 Å.; the compounds with an appreciable amount of electron transfer, which necessitates an interpolation of p- or d-character, show larger discrepancies.

The observed pattern of electron transfer is in agreement with Pauling's theory¹² in that boron, although a hypoelectronic atom, tends to transfer electrons to the less electronegative and likewise hypoelectronic atoms magnesium and aluminum. The tendency for boron to donate electrons decreases as the hypoelectronic character of the other atom decreases (and its electronegativity increases), until the buffer atom chromium, with an electronegativity approximately equal to that of boron, is able to transfer a relatively large amount of charge to boron.

The derived value for the single-bond radius of boron, 0.77 Å., is somewhat smaller than the value 0.80 Å. reported by Hedberg⁹ for boron hydrides and related compounds. This discrepancy is probably to be expected in view of the great dissimilarity in the types of structures involved. In particular, the AlB_2 structure, with well-defined layers and consequent anisotropy of bonding, would be open to strain and deformation of bonds; perhaps more important is the high coordination of boron (9-fold) compared to that in the more co-valent type structures. A complete study on other metal-boron type compounds would throw some light on the bonding characteristics of boron.

The authors are indebted to the Office of Naval Research for financial help in this investigation and to Professor Linus Pauling for valuable discussions and critical comments.

(12) L. Pauling, *Proc. Natl. Acad. Sci.*, **36**, 533 (1950).

PASADENA, CALIFORNIA

(11) J. Russell, R. Hirst, F. A. Kanda and A. J. King, *Acta Cryst.*, **6**, 870 (1953).

[CONTRIBUTION FROM THE OAK RIDGE NATIONAL LABORATORY, CHEMISTRY DIVISION]

Determination of Activity Coefficients by Ultracentrifugation. Ultracentrifugation of Uranyl Fluoride Solutions^{1a,b}

BY JAMES S. JOHNSON, KURT A. KRAUS AND T. FRASER YOUNG^{1c}

RECEIVED SEPTEMBER 24, 1953

Equilibrium ultracentrifugation of two-component systems is discussed from the point of view of determination of stoichiometric activity coefficients. Ultracentrifugation of cadmium iodide solutions was found to yield activity coefficients which were in satisfactory agreement with those in the literature. By ultracentrifugation, activity coefficients of UO_2F_2 in aqueous solution were obtained which were similar to those found by freezing point depressions, thus supporting the earlier hypothesis of a monomer-dimer equilibrium. The dimerization constant appears to increase slightly with temperature, indicating a small and positive heat of dimerization. Ultracentrifugation of UO_2F_2 in KF solutions indicates that excess fluoride ions increase the stability of the dimer considerably.

It has been pointed out, particularly by Peder-

sen² and Drucker,³ that ultracentrifugation to equilibrium can be used for the determination of activity coefficients of solutes, since at equilibrium there is essentially a balance between the chemical and centrifugal potentials. Pedersen used activity coefficients of various solutes in the literature to calculate the (known) molecular weights;

(1) (a) This document is based on work performed for the Atomic Energy Commission at the Oak Ridge National Laboratory. (b) Table I has been deposited as Document number 4146 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D. C. A copy may be secured by citing the Document number and by remitting in advance \$1.25 for photoprints, or \$1.25 for 35 mm. microfilm by check or money order payable to: Chief, Photoduplication Service, Library of Congress. (c) George Herbert Jones Chemical Laboratory, University of Chicago. Consultant to the Chemistry Division, Oak Ridge National Laboratory.

(2) (a) K. O. Pedersen, *Z. physik. Chem.*, **A170**, 41 (1934); (b) T. Svedberg and K. O. Pedersen, "The Ultracentrifuge," The Clarendon Press, Oxford, England, 1940, p. 53.

(3) C. Drucker, *Z. physik. Chem.*, **A180**, 359 (1937).